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TECHNICAL REPORT ARCCB-TR-89031

DETERMINATION OF PHOSPHORIC AND SULFURIC ACIDS IN POLISHING SOLUTIONS BY ACID-BASE TITRATION USING A pH METER

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NOVEMBER 1989

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1. REPORT NUMBER: ARCCB-TR-89031	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): DETERMINATION OF PHOSPHORIC AND SULFURIC ACIDS IN POLISHING SOLUTIONS BY ACID-BASE TITRATION USING A pH METER	5. TYPE OF REPORT & PERIOD COVERED: Final
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): Samuel Sopok	8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS: U.S. Army ARDEC, Benet Laboratories, SMCAR-CCB-TL, Watervliet, NY 12189-4050	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: AMCMS No. 6126.23.1BL0.0, PRON No. 1A92ZNACNMSC
11. CONTROLLING OFFICE NAME AND ADDRESS: U.S. Army ARDEC, Close Combat Armaments Center, Picatinny Arsenal, NJ 07806-5000	12. REPORT DATE: November 1989
	13. NUMBER OF PAGES: 12
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Submitted to Plating and Surface Finishing.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Chemical Analysis
Phosphoric Acid
Sulfuric Acid
Alloy Steel Polishing Solutions
Chromium Plating
Acid-Base Titration
pH Meter

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The chemical literature lacks an acceptable analytical method for adequately monitoring phosphoric and sulfuric acids in alloy steel polishing solutions during the polishing process. In this report, an improved method is presented that provides acceptable analysis and monitoring of these acids. The typical operating ranges of these acid constituents are 640 to 730 g/l phosphoric acid and 795 to 895 g/l sulfuric acid. The resulting precisions are in the range of 0 to 8 g/l, providing adequate monitoring of these polishing solutions supported by six years of testing.

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ACKNOWLEDGMENTS

Special thanks are given to Ellen Fogarty and Rose Neifeld of Benet Laboratories for their respective word processing and technical editing work on this manuscript.

INTRODUCTION

The chemical literature lacks an acceptable analytical method for adequately monitoring phosphoric and sulfuric acids in alloy steel polishing solutions during the polishing process. Lack of optimization of these polishing solutions causes serious problems for the alloy steel polishing and chromium plating industries such as poor quality products and wasted resources.

An alloy steel polishing solution contains approximately a 50:50 volume ratio of concentrated phosphoric and sulfuric acids.

One analytical method to determine phosphoric and sulfuric acids in alloy steel polishing solutions is a sodium hydroxide titrant and a methyl orange/phenolphthalein indicator system to detect the respective endpoints for these acids (ref 1). The problem associated with this method is that the color changes at the endpoints for the polishing sample solutions are gradual and indistinct. This is shown in the literature in the acid-base titration chapter of Fritz and Schenk (ref 2) where the endpoints with these two indicators vary by plus or minus one pH unit depending on the chemistry of the solutions. Relative precisions of this method are in the range of 2 to 3 percent.

Another chemical analysis method to determine phosphoric and sulfuric acids in alloy steel polishing solutions is a sodium hydroxide titrant where titration curves are acquired for each sample solution. This method is not given anywhere in the literature, but it can be derived from basic principles (ref 2). Inflection points or first derivatives of the titration curves provide the endpoints of each acid titration. The problem associated with this method is that acquiring titration curves is a time-consuming and tedious procedure which is unacceptably slow for this application. Automated titrators were used to make

References are listed at the end of this report.

the procedure less time-consuming and less tedious, but they do not locate the endpoints precisely for this two-acid system as experienced by this author. Relative precisions of this method are in the range of 0 to 2 percent.

The theoretical endpoints and pH values to determine phosphoric and sulfuric acids in the polishing solutions by sodium hydroxide titrant can be calculated to 0.1 pH unit from data in the acid-base titration chapters of Fritz and Schenk (ref 2) and Peters et al. (ref 3) for these chemical conditions.

The simple method presented in this report provides acceptable analysis and control of these acids in the polishing solution. The method uses the sodium hydroxide titrant, the calculated theoretical endpoint values, and a pH meter to determine these acids. Relative precisions of this method are in the range of 0 to 1 percent. This method combines the speed of the indicator method with the precision of the titration curve method.

EXPERIMENTAL PROCEDURE

Strict analytical chemistry methods and procedures are followed throughout this experimental procedure section. An excellent source of reference for the methods and procedures is by Fritz and Schenk (ref 2).

Three analytical reagent grade standard solutions are required. The first solution is a 40 ± 0.01-g/l sodium hydroxide solution that is standardized with primary standard potassium acid phthalate as described in References 2 and 4. The second is a 4 ± 0.05-pH unit standard buffer solution, and the third is a 10 ± 0.05-pH unit standard buffer solution. These buffer solutions are standardized against the primary standard buffer solutions in Table 11-1 of Reference 3.

Preparation of a polishing solution sample for titration analysis requires that 10 milliliters (ml) of the sample solution is pipetted into a 250-ml volumetric flask which is filled to the mark with deionized water. Then 25 ml of the diluted sample solution is pipetted from the flask and diluted to about the 200-ml mark with deionized water in a 400-ml beaker. A stirring bar is added to the beaker.

The pH meter is calibrated by using both the 4 and 10 pH buffer solutions. The pH readings for each buffer solution may not vary by more than 0.10 pH unit.

The solution is titrated using the sodium hydroxide titrant to endpoints at 4.50 ± 0.10 and 9.70 ± 0.10 pH units recording the amount of titrant dispensed at the respective endpoints in milliliters as "reading A" and "reading B."

All standard and sample solutions are analyzed in triplicate. Phosphoric and sulfuric acid concentrations in the samples are calculated by normal chemical stoichiometry.

RESULTS AND DISCUSSION

Experimental acid-base titration data are presented in Table I for sample polishing solutions one and two. The acid-base titration consists of the following five equations to various definite extents:

$$H_3PO_4 + NaOH \text{ <--> } NaH_2PO_4 + H_2O \quad (1)$$

$$NaH_2PO_4 + NaOH \text{ <--> } Na_2HPO_4 + H_2O \quad (2)$$

$$Na_2HPO_4 + NaOH \text{ <--> } Na_3PO_4 + H_2O \quad (3)$$

$$H_2SO_4 + NaOH \text{ <--> } NaHSO_4 + H_2O \quad (4)$$

$$NaHSO_4 + NaOH \text{ <--> } Na_2SO_4 + H_2O \quad (5)$$

The calculations for determining the concentrations of phosphoric and sulfuric acids in the sample solutions are

$$g/l\ H_3PO_4 = (A - B)(C)(98) \quad (6)$$

$$g/l\ H_2SO_4 = (2A - B)(C)(49) \quad (7)$$

where

A = "reading A"

B = "reading B"

C = titrant normality

The constant values in Eqs. (6) and (7) are the combined result of many constants (refs 2-4).

Using Eqs. (6) and (7), the respective phosphoric and sulfuric acid values for sample solution one in Table I are 666 and 799 g/l. Likewise, using the same equations, the respective phosphoric and sulfuric acid values for sample solution two in Table I are 718 and 868 g/l.

It is useful to evaluate the variations in precision for the materials and methods used. Tables II through VII present the data for the 10- and 25-ml class-A pipets, 250-ml class-A volumetric flasks, pH = 4 and 10 buffer solutions, pH meter readings at pH = 4 and 10, 40-g/l sodium hydroxide titrants, and 50-ml class-A burets, respectively.

The data obtained by this method are sufficient to adequately monitor the phosphoric and sulfuric acids in the alloy steel polishing process, thus providing efficient use of resources. The typical operating ranges of the respective phosphoric and sulfuric acids in the polishing solutions are 640 to 730 g/l and 795 to 895 g/l. The resulting precisions are in the range of 0 to 8 g/l, providing adequate monitoring of these solutions supported by six years of testing.

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2. J. Fritz and G. Schenk, Quantitative Analytical Chemistry, Fifth Edition, Allyn and Bacon, Inc., Boston, MA, 1987.
3. D. Peters, J. Hayes, and G. Hieftje, Chemical Separations and Measurements: Theory and Practice of Analytical Chemistry, W. B. Saunders Company, Philadelphia, PA, 1974.
4. R. Brumblay, Quantitative Analysis, Harper and Row Publishers, New York, 1972.

TABLE I. EXPERIMENTAL TITRATION DATA FOR SAMPLE POLISHING SOLUTIONS ONE AND TWO

Sample One Replicates	Titrant Used (ml) Reading A	Titrant Used (ml) Reading B
1	23.15	29.90
2	23.10	29.95
3	23.15	29.95
X(avg)	23.13	29.93
Sample Two Replicates	**Titrant Used (ml) Reading A**	**Titrant Used (ml) Reading B**
1	25.05	32.40
2	25.05	32.40
3	25.05	32.35
X(avg)	25.05	32.38

TABLE II. PRECISION OF A 10- AND 25-ml CLASS-A PIPET

Replicate	10-ml Pipet Volume (ml)*	25-ml Pipet Volume (ml)*
1	10.03	25.04
2	10.00	24.99
3	9.98	24.96
4	9.99	25.03
5	9.98	25.01
6	10.04	25.05
X(avg)	10.00	25.01
Sn	0.02	0.03

*Volumes are calculated from the weight-volume relationship of a pipetted deionized water solution corrected for temperature.

TABLE III. PRECISION OF A 250-ml CLASS-A VOLUMETRIC FLASK

Replicate	Volume (ml)*
1	249.57
2	249.37
3	249.64
4	249.41
5	249.51
6	249.62
X(avg)	249.52
Sr	0.10

*Volumes are calculated from the weight-volume relationship of the contained deionized water solution corrected for temperature.

TABLE IV. PRECISION OF pH = 4 AND 10 BUFFER SOLUTIONS

Replicate	pH = 4 Buffer Solution*	pH = 10 Buffer Solution*
1	4.06	9.96
2	4.06	9.99
3	4.02	10.05
4	3.98	10.06
5	4.02	9.94
6	3.97	10.00
X(avg)	4.01	10.00
Sn	0.03	0.04

*The pH values are standardized against primary standard buffer solutions in the potentiometry chapter of Reference 3 using a pH meter.

TABLE V. PRECISION OF READINGS AT pH = 4 AND 10

Replicate	pH = 4 Readings*	pH = 10 Readings*
1	4.04	10.00
2	3.98	10.02
3	4.02	10.04
4	4.04	10.05
5	4.03	10.02
6	4.05	10.01
X(avg)	4.03	10.02
Sn	0.02	0.02

*The pH values are standardized against primary standard buffer solutions in the potentiometry chapter of Reference 3 using a pH meter.

TABLE VI. PRECISION OF A 40-g/l SODIUM HYDROXIDE STANDARD SOLUTION

Replicate	Sodium Hydroxide (g/l)*
1	40.01
2	40.00
3	39.99
4	39.99
5	40.01
6	40.00
X(avg)	40.00
Sn	0.01

*Sodium hydroxide concentrations are calculated by titration using the primary standard potassium acid phthalate for standardization.

TABLE VII. PRECISION OF A 50-ml CLASS-A BURET

Replicate	Volume (ml)*
1	24.94
2	24.98
3	25.02
4	25.05
5	24.98
6	25.05
X(avg)	25.00
Sn	0.04

*Volumes are calculated from the weight-volume relationship of a contained deionized water solution corrected for temperature at the point one-half full--25 ml.

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